



# PATENT SPECIFICATION

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## PROVISIONAL SPECIFICATION

### Improvements in Treatment and Production of Esters

We, VICTOR WOLF LIMITED, a British Company, of Victoria Works, Croft Street, Clayton, Manchester, 11, in the County of Lancaster, and RICHARD 5 ROWE, a British Subject, of the said Company's address, do hereby declare the nature of this invention to be as follows:—

This invention relates to improvements 10 in the production of esters and particularly either by the alcoholysis of esters or by esterification of acids with the use of halogen hydracids as catalysts.

In the alcoholysis of esters, especially 15 of glycerides, anhydrous hydrochloric acid has been known as a very effective catalyst. However, the necessity to produce the gaseous product at first in a special generator before it is introduced 20 into the reaction-mixture or into one of its components has generally prevented up to now the use of hydrochloric acid as catalyst for alcoholysis in practice.

It is possible, under certain conditions, 25 to use concentrated aqueous hydrochloric acid instead of the gaseous but in this case a certain degree of saponification is unavoidable, and the subsequent refining of the reaction product becomes 30 necessary.

We have found that all these difficulties can be avoided if hydrochloric acid— 35 or other halogen hydracid—is generated from a metal halide within the alcohol used for the process or still better within the reaction mixture by addition of a mineral acid i.e. if concentrated sulphuric acid is added to a mixture of 40 ester, alcohol and a metal halide. In a preferred form the invention consists in generating the acid *in situ* by interaction between a metal halide which is soluble in the reaction mixture or at least in the alcohol used and an acid such 45 as concentrated sulphuric acid or concentrated phosphoric acid which is capable of liberating the halogen hydracid and forming a salt which is insoluble or sparingly soluble in the reaction mixture under the prevailing 50 conditions.

Metal halides, especially the chlorides of lithium, calcium, strontium and zinc,

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and aliphatic alcohols containing at most five carbon atoms are therefore especially 55 suited for the process.

It is generally not necessary to work at elevated temperatures; thus for example, the generation of hydrochloric acid 60 simultaneously with the alcoholysis of oils which are soluble in alcohols, say castor oil, can be performed at room temperature, whereby the same small quantities of alcohols can be used as mentioned in British Patent No. 563,481. 65

The process is preferably carried out in the absence or substantial absence of water, but small quantities such as are present for example in the form of 70 crystal-water in some of the metal halides do not appear to be objectionable.

The quantity of metal halides and the equivalent amount of acid may vary, but generally such quantities are used that 75 the halogen hydracid produced amounts to 1–2% of the reaction mixture. Should it be desirable to avoid any side-reaction of the sulphuric or the like acid, a slight excess of the metal halide can be provided. The amount of alcohol may 80 be large, as in the well known processes or relatively small as in British Patent No. 563,481.

#### EXAMPLE.

A solution of 100 parts of anhydrous 85 calcium chloride in 750 parts of *n*-butanol is mixed with 1000 parts of castor oil. Then 270 parts of concentrated sulphuric acid are added gradually while stirring and cooling. 90 The solution becomes more and more turbid and calcium sulphate separates out. After a few days the calcium sulphate is filtered and the filtrate washed repeatedly with water which may contain some 95 common salt in order to remove the mineral acid, the glycerine and the surplus of butanol. Finally the oil is distilled in vacuum whereby about 1000 100 parts of an oil consisting of the *n*-butyl esters of the castor oil fatty acids are obtained. In this example all parts are by weight.

The described process offers the same advantages in the case of the production 105 of esters by treatment of the acids them-

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selves with alcohols in presence of halogen hydracids. Thus for example butyl-ricinoleate can be produced by the addition of sulphuric acid to a mixture of 5 castor oil fatty acids and butanol and calcium chloride.

The invention is applicable, for

example, to the production of alkyl esters of fatty acids from natural oils or from fatty acids.

Dated this 14th day of March, 1945.

W. P. THOMPSON & CO.  
12, Church Street, Liverpool, 1,  
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## COMPLETE SPECIFICATION

### Improvements in Treatment and Production of Esters

We, VICTOR WOLF LIMITED, a British Company, of Victoria Works, Croft Street, Clayton, Manchester, 11, in the County of Lancaster, and RICHARD ROWE, a British Subject, of the said Company's address, do hereby declare the nature of this invention and in what manner the same is to be performed, to be particularly described and ascertained in and by the following statement:—

This invention relates to improvements in the production of esters of organic carboxylic acids employing hydrogen halide as the catalyst and is more especially suitable for the production of esters by alcoholysis of esters or by esterification of acids.

In the alcoholysis of esters, especially of glycerides, anhydrous hydrochloric acid has been known as a very effective catalyst. However, the necessity of first producing the gaseous product in a special generator before it is introduced into the reaction-mixture or into one of its components has generally prevented up to now the use of hydrochloric acid as catalyst for alcoholysis in practice.

It is possible, under certain conditions, to use concentrated aqueous hydrochloric acid instead of the gaseous hydrogen chloride, but in this case a certain degree of saponification is unavoidable, and the subsequent refining of the reaction product becomes necessary.

It has now been found that these difficulties can be substantially avoided according to the present invention wherein esters of organic carboxylic acids are produced by alcoholysis or esterification with an aliphatic alcohol of less than six carbon atoms employing hydrogen halide as catalyst, the hydrogen halide being produced within the reaction mixture by interaction between a metal halide which is soluble in at least one component of the reaction mixture and a mineral acid which forms with the metal of the halide a salt which is insoluble or sparingly soluble in the reaction mixture under the prevailing conditions.

Halides, and especially chlorides of lithium, calcium, magnesium, strontium, zinc, or bromides such as sodium and calcium bromides can be used. The

alcohol-soluble halides of the alkaline earth metals, especially calcium chloride or magnesium chloride are the preferred salts and with any of these sulphuric acid or phosphoric acid may be employed for liberating the hydrogen halide.

Any ester of organic carboxylic acid may be used for the alcoholysis which is soluble in the aliphatic alcohol employed, at least when warmed, especially natural oils such as for example, castor oil which is easily soluble in all aliphatic alcohols.

It is generally not necessary to work at elevated temperatures; thus, for example, the generation of hydrogen halide simultaneously with the alcoholysis of oils which are soluble in alcohols, say castor oil, can be performed without heating.

The process is preferably carried out in the substantial absence of water, but small quantities such as are present for example in the form of water of crystallisation in some of the halides are not objectionable to the alcoholysis.

Generally equivalent amounts of the halide and acid are used, and such a quantity that the hydrogen halide produced amounts to 1—2% by weight of the reaction mixture. Should it be desirable to avoid any side-reaction with the sulphuric or other acid used to liberate the hydrogen halide, an excess of the halide can be provided.

The amount of alcohol may be large, as in the well known processes or relatively small as in British Specification No. 563,481.

The described process offers the same advantages in the case of the production of esters by treatment of the organic carboxylic acids themselves with aliphatic alcohols, for example, primary alcohols in presence of hydrogen halides. Thus, for example, butyl ricinoleate can be produced by the addition of sulphuric acid to a mixture of castor oil fatty acids and butanol and calcium chloride.

The invention is applicable to the production of alkyl esters of fatty acids from natural oils or from fatty acids.

The invention will be further described by reference to the following four examples but it must be understood that

these examples are included by way of illustration and the invention is not limited thereto:—

#### EXAMPLE 1.

- 5 1000 g. castor oil are mixed with a solution of 55 g. anhydrous calcium chloride in 750 g. of *n*-butanol. Then 50 g. of concentrated sulphuric acid are added gradually while stirring and cooling. The solution becomes more and more turbid and calcium sulphate separates out. After a few days the calcium sulphate is filtered and the filtrate washed repeatedly with water—  
15 which may contain common salt—in order to remove the mineral acid, the glycerine and the surplus of the butanol. Finally the oil—about 1100 g.—is distilled in vacuum whereby 1000—1100 g. of colourless oil consisting of the *n*-butyl esters of the castor oil fatty acids are obtained. (B.p. 217—235° at 3 mm.).

#### EXAMPLE 2.

- 25 A solution of 35 g. commercial anhydrous magnesium chloride containing about 20% water in 500 g. *n*-butanol is mixed with 500 g. olive oil. 27 g. concentrated sulphuric acid are added gradually; finally the mixture is heated on the water bath for about 7 hours. After cooling down the clear solution is separated from the magnesium sulphate by filtration and worked up according to Example 1. 550 g. raw esters are obtained. By distillation in vacuum (3 mm.) 510 g. of a mixture of the *n*-butyl esters of the olive oil fatty acids distil over at 205°—219° C.

#### EXAMPLE 3.

- 40 60 g. calcium chloride are dissolved in 650 g. propanol and mixed with 1000 g. castor oil. After addition of 36 g. phosphoric acid (s.g. 1.75) calcium-phosphate separates out gradually. After four days standing the reaction mixture is stirred with limestone and filtered when neutral. The propanol is distilled off and finally the residue distilled in vacuum. The distillate, about 1000 g., consists of the propyl esters of the castor oil fatty acids (saponification value (S.V.) 165).

#### EXAMPLE 4.

- 55 90 g. concentrated sulphuric acid are added gradually to a solution of 180 g. sodium bromide in 2500 g. methanol. After 1 hour standing the sodium sulphate is filtered, 3000 g. linseed fatty acids are mixed with the filtrate and the whole stirred for 24 hours at room temperature. The reaction mixture is then poured into water and washed repeatedly

with warm water until the whole hydrobromic acid is removed. The oil is dried and finally subjected to a vacuum distillation. The distillate (b.p. 180—192° C. at 2.5 mm.) is a mixture of the methyl esters of the linseed fatty acids. (Acid value (A.V.) 190).

#### EXAMPLE 5.

0.52 kg. strontium bromide are dissolved in 5 kg. methylated spirit 72 o.p., and 1.7 kg. benzoic acid are added to the solution. Finally 0.2 k.g. conc. sulphuric acid are stirred in gradually, whereby strontium-sulphate is precipitated. The mixture is now heated to the boiling point for 6 to 7 hours. After cooling down calcium carbonate is added, and when the solution is neutral, it is filtered. Then the ethanol is distilled off and the residue repeatedly washed to remove the bromide and any benoic acid still present. Finally the product is distilled. The distillate, 1.65 kg., consists of ethylbenzoate.

It will thus be apparent that essential steps comprising the invention can be carried out as follows:—

The ester or the fatty acid used as raw material and the metal halide are dissolved in the alcohol whereafter the mineral acid is added which sets free the hydrogen halide; subsequent treatment corresponds to the procedure used in the alcoholysis of esters by means of hydrogen halides. Alternatively, the reaction mixture can be prepared wherein the metal halide is first dissolved in the alcohol and the hydrogen halide set free by addition of the acid, subsequently, the ester or fatty acid is added thereto, with or without previous filtration of the precipitated salt.

Having now particularly described and ascertained the nature of our said invention and in what manner the same is to be performed, we declare that what we claim is:—

1. A process for the production of esters of organic carboxylic acids with an aliphatic alcohol of less than six carbon atoms either by esterification of said organic carboxylic acids or by alcoholysis of esters of such acids with other alcohols employing hydrogen halide as the catalyst in which the hydrogen halide is produced in at least one component of the reaction mixture by interaction between a metal halide which is soluble in at least one component of the reaction mixture and a mineral acid which forms with the metal of the halide a salt which is insoluble or sparingly soluble in the said reaction mixture under the prevailing conditions.

2. A process for the production of esters as claimed in claim 1 in which the hydrogen halide is produced within the alcohol before the latter is mixed with the fatty acid esters or the fatty acids.

3. A process for the production of esters of organic carboxylic acids as claimed in claim 1 in which the hydrogen halide is produced within the reaction mixture.

4. A process for the production of esters of organic carboxylic acids as claimed in claims 1—3 in which the hydrogen halide is produced by interaction between an alkaline earth halide such as calcium or magnesium chloride and either sulphuric or phosphoric acids.

5. A process as claimed in claim 1 for the production of esters of organic car-

boxylic acids by alcoholysis of oils of natural origin such as glycerides.

6. A process as claimed in claim 5 in which the starting material is castor oil.

7. A process as claimed in any of claims 1 to 6 in which the alcohol used is a primary aliphatic alcohol having less than six carbon atoms.

8. A process for the production of esters of organic carboxylic acids as herein particularly described with reference to examples 1 to 5.

9. Esters of organic carboxylic acids when produced according to any of the processes hereinbefore claimed.

Dated this 12th day of March, 1946.

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